

# Vacuum Tribological Behaviour of Self-Lubricating Quasicrystalline Composite Coatings

F.J. García de Blas, A. Román, C. de Miguel, F. Longo, R. Muelas, and A. Agüero  
National Institute of Aerospace Technology (INTA), Madrid, Spain

## Abstract

---

High-temperature-resistant self-lubricating coatings are needed in space vehicles for components that operate at high temperatures and/or under vacuum. Thick composite lubricant coatings containing quasicrystalline alloys as the hard phase for wear resistance can be deposited by a thermal spray technique. The coatings also contain lubricating materials (silver and  $\text{BaF}_2$ - $\text{CaF}_2$  eutectic) and NiCr as the tough component. This paper describes the vacuum tribological properties of TI1103, a coating of this type, with a very good microstructural quality. The coating was deposited by high-velocity oxygen fuel spraying and tested under vacuum using a pin-on-disc tribometer. Different loads, linear speeds, and pin materials were studied. The pin scars and disc wear tracks were characterised using a combination of scanning electron microscopy and energy dispersive spectrometry. A minimum mean steady friction coefficient of 0.32 was obtained when employing an X750 Ni superalloy pin in vacuum conditions under 10 N load and 15 cm/s linear speed, showing moderate wear of the disc and low wear of the pin.

## Keywords

---

quasicrystalline alloys, composite powder, self-lubricating coatings, vacuum pin-on-disc test, HVOF, friction, wear

## INTRODUCTION

---

High-temperature-resistant self-lubricating coatings are needed in space vehicles for components that operate at high temperatures and/or under vacuum. These coatings should exhibit low shear strength and maintain their chemical stability at extreme temperatures and in the space environment.<sup>1</sup>

An in-space instrument (TriboLAB) capable of evaluating some tribological properties as well as the durability of solid lubricant coatings has been built as part of a joint Spanish-British effort supported by the European Space

Agency (ESA).<sup>2</sup> This instrument will be integrated into the EuTFF (European Technology Exposure Facility) on the International Space Station. The coatings considered in the present work are being optimised for testing in TribolAB. If successful, these coatings could be employed in reusable space vehicle applications, such as elevon hinges, where temperatures of 700°C are reached during re-entry into the Earth's atmosphere.<sup>1</sup> These coatings should also be capable of providing effective lubrication at lower temperatures since 'cold start' operation may be necessary,<sup>3</sup> even in the space environment.

Self-lubricating composite coatings containing solid lubricants in a hard matrix can be designed to behave adequately in the situations mentioned above. For instance, NASA's Lewis Research Center has developed self-lubricating composite coatings for terrestrial use comprising hard materials such as chromium carbide and solid lubricant additives such as silver and  $\text{BaF}_2$ - $\text{CaF}_2$  eutectic in a NiCr matrix. These coatings are applied by plasma and high-velocity oxygen fuel (HVOF) thermal spraying. They significantly reduce the friction coefficient and improve wear resistance over a wide temperature range.<sup>4-6</sup>

Thick composite lubricant coatings containing quasicrystalline (QC) alloys as the hard phase for wear resistance have been deposited by plasma and HVOF spraying. QC alloys show promising tribological characteristics<sup>7</sup> exhibiting a combination of appropriate antifriction properties, namely, low friction coefficient, high hardness, and high yield strength under compression,<sup>8,9</sup> thermal expansion coefficients close to those of metals, high thermal stability, low thermal conductivity, and good oxidation and hot corrosion resistance.<sup>10</sup> The coatings also comprise lubricating materials (silver and  $\text{BaF}_2$ - $\text{CaF}_2$  eutectic) and NiCr as the tough component.

Composite coatings of different composition have been developed and optimised in order to improve the microstructure of the coatings and the tribological behaviour.<sup>2,11,12</sup> This paper describes the vacuum tribological properties of TH103 (AlCoFeCr, NiCr, Ag,  $\text{CaF}_2$ ,  $\text{BaF}_2$ ), deposited by HVOF spraying, which has shown the best tribological properties so far. As previously described,<sup>2</sup> TH103 exhibits a very good microstructural quality (low porosity and uniform phase distribution) and the main phases present in the powder are maintained in the coating. The coating was tested under vacuum using a pin-on-disc tribometer at AMTT-ARC (Aerospace and Space Materials Technology Test House - Austrian Research Centres) in Seibersdorf (Austria). Different loads, linear speeds, and pin materials were studied.

## **EXPERIMENTAL: Materials**

The disc substrate was X750 Ni superalloy. The composition of this material (in wt.%) is as follows: Cr, 16; Fe, 8; Ti, 2.5; Nb, 1; Co, 1; Al, 0.8; Mn, 0.35; Si, 0.35; Ni, balance.

The spray powder for TH103 was prepared by mixing AlCoFeCr powder (SNMI Cristome 100, 20–53  $\mu\text{m}$ ), NiCr (Sulzer Metco 43F-NS, <56  $\mu\text{m}$ ), Ag (SEMP, <56  $\mu\text{m}$ ), and  $\text{BaF}_2$ – $\text{CaF}_2$  eutectic (made in house from Aldrich fluorides, <45  $\mu\text{m}$ ).

### *Deposition*

---

The coating was deposited by HVOF spraying, using a Sulzer Metco Diamond Jet Hybrid unit (model A-3120) mounted on a six-axes robot (ABB) and fed by a twin rotation powder feeder.

### *Characterisation*

---

The samples were characterised by optical and electron microscopy (JEOL JSM-840 equipped with a KEVEX energy dispersive spectrometry (EDS) micro-analyser).

Hardness measurements were carried out using a Future-Tech Vickers indenter under a 200 g load, on polished cross-sections.

### *Wear tests*

---

The coating was tested using a high-vacuum pin-on-disc tribometer at AMTT-ARC, employing four different loads of 1, 2, 5, and 10 N and two linear speeds of 1.5 and 15 cm/s at  $10^{-5}$  mbar. Three different pin materials (X 750, 100Cr6, and  $\text{Al}_2\text{O}_3$ ) were used.

The roughness of the pins and discs and the pin scars and disc wear tracks were measured with a Taylor–Hobson pneumo-profilometer with a 2  $\mu\text{m}$  diamond cone stylus tip. The pin scars and disc wear tracks produced during the pin-on-disc tests were also studied using a combination of scanning electron microscopy and energy dispersive spectrometry (SEM-EDS).

## *RESULTS AND DISCUSSION: Microstructure of the coating*

---

Several composite coatings were developed and optimised in order to improve the microstructure of the coatings and the tribological behaviour.<sup>2,11,12</sup> Among these coatings, HVOF TH103 showed the best microstructure, as can be observed in **Figure 1** (see facing p. 108).

The HVOF TH103 coating shows a very good microstructural quality (low porosity and uniform phase distribution) and the main phases present in the powder are maintained in the coating.<sup>2</sup>

**Table 1 Vacuum pin-on-disc test wear data for HVOF TH103 coating**

Pin material	L (N)	$P_{\text{Hertz}}$ (GPa)	V (cm/s)	Cycles	$\mu_{\text{st}}$	$k_d$ ( $10^{-6} \text{ mm}^3/\text{N m}$ )	$k_p$
X750 <sup>†</sup>	1	0.66	1.5	6167	0.80	ND <sup>‡</sup>	8.6
X750	1	0.66	1.5	6006	0.67	407	10.4
X750	5	1.14	1.5	6003	0.59	509	10.5
X750	10	1.43	1.5	3071	0.49	400	36.7
Al <sub>2</sub> O <sub>3</sub>	2	1.00	1.5	6005	0.65	305	2.9
100Cr6	2	0.82	1.5	1817	0.57	339	2.1
X750	2	0.84	1.5	1612	0.57	290	3.5
X750	5	1.14	1.5	6003	0.59	509	10.5
X750	10	1.43	1.5	3071	0.49	400	36.7
X750	10	1.43	15	39,875	0.32	76.2	1.0
X750	5	1.14	15	31,810	0.50	539	11.3

\* $P_{\text{Hertz}}$ : Hertzian pressure;  $\mu_{\text{st}}$ : mean steady friction coefficient;  $k_d$ : disc wear coefficient;  $k_p$ : pin wear coefficient.

<sup>†</sup>Test at atmospheric pressure.

<sup>‡</sup>ND: not detectable.

### Tribological behaviour of the coating

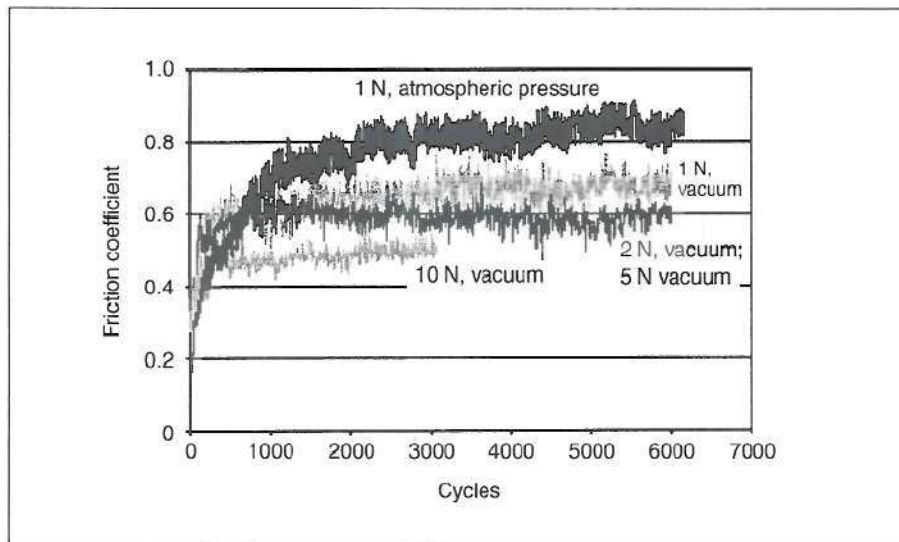
The microhardness of the coating ranged from 600 to 625 HV<sub>0.2</sub>, confirming previous results.<sup>11</sup>

Table 1 gives the wear and friction coefficients ( $k$  and  $\mu$ ) for the test coating under different conditions as well as the Hertzian pressure,  $P_{\text{Hertz}}$ , calculated by dividing the applied load by the contact area. The wear coefficients of the coated discs and pins ( $k_d$  and  $k_p$  respectively) were calculated by dividing the measured wear volume by the load applied and the sliding distance.

Three different pin materials (X750 Ni superalloy, 100Cr6 steel, and Al<sub>2</sub>O<sub>3</sub>) were used. 100Cr6 steel is commonly used in tribological applications, and Al<sub>2</sub>O<sub>3</sub> is a ceramic material with potential for high-temperature tribological applications.

The friction coefficient for the X750 material rubbing against an X750 pin in the pin-on-disc test was 0.9 under atmospheric conditions, whereas for a TH103-coated disc also rubbing against an X750 pin the friction coefficient decreased to 0.8, indicating that the coating behaves as a lubricant. (Time constraints did not allow a full comparison to be made with wear data for uncoated discs.)

**Figure 2** Friction coefficient for different loads in tests with HVOF TH103 coating and X750 pins at 1.5 cm/s linear speed



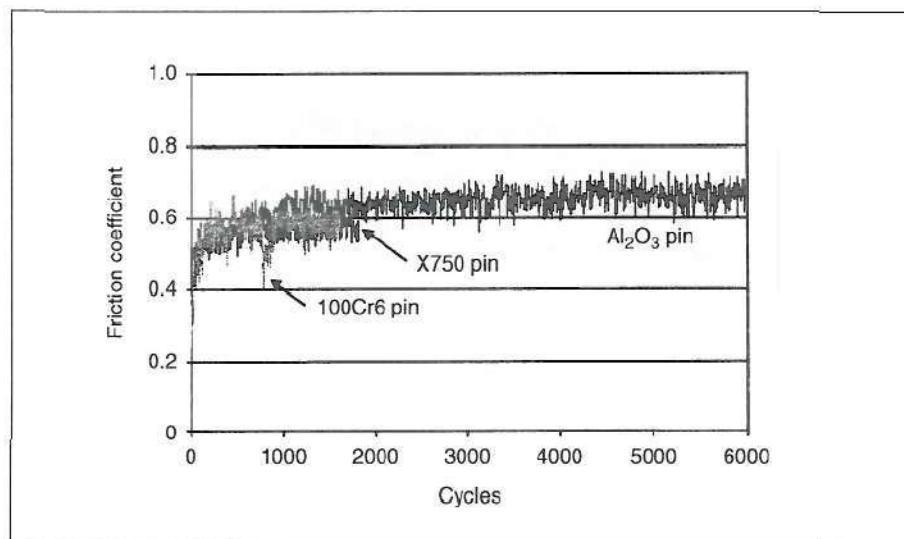
#### *Influence of pressure and applied load*

**Figure 2** shows the influence of load on the friction coefficient of the HVOF TH103 coating as a function of the number of cycles in tests using X750 pins. The friction coefficient at atmospheric pressure and under 1 N load is also included in order to compare the friction coefficient behaviour at atmospheric pressure and in vacuum.

SEM-EDS mapping of the test pins indicates that at atmospheric pressure no coating transfer to the pin takes place.<sup>11</sup> However, under vacuum, for all three loads some coating material was transferred to the pin and formed a self-lubricating transfer film on its surface, as can be seen in **Figure 3** (see facing p. 108). This could very well explain the lower friction coefficients obtained in vacuum. Other authors have indicated that oxidation of the coating may prevent film transfer at atmospheric pressure, thus explaining the absence of wear on the coated disc;<sup>13</sup> however, debris from the pin was found on the disc track at atmospheric pressure.

As to the influence of load, see **Figure 2**, the friction coefficient decreased as the applied load increased under vacuum. This effect, already observed for metal-MoS<sub>2</sub> composite coatings, is not fully understood<sup>14</sup> but could be due to a greater amount of self-lubricant transfer from the coated disc to the pin at higher applied loads or to a greater lubricated contact area. There was no evidence of

**Figure 5** Influence of the pin material on the friction coefficient for the HVOF TH103 coating at 2 N load and 1.5 cm/s linear speed under vacuum



transfer of material from the pin to the disc for the three applied loads (Figure 4, see facing p. 109) and the discs suffered moderate/high wear ( $10^{-4} \text{ mm}^3/\text{N m}$ ), but only related to coating loss and never reaching the substrate. The pins showed moderate wear ( $10^{-5} \text{ mm}^3/\text{N m}$ ).

#### Influence of pin materials

Figure 5 shows the friction coefficients for three different pin materials ( $\text{Al}_2\text{O}_3$ , X750, and 100Cr6) rubbing against coated discs. Both X750 and 100Cr6 pins exhibited the same friction coefficient, although 100Cr6 is harder than X750 (700 HV vs. 400 HV), probably indicating that the lubrication provided by the coating overcame the expected higher wear produced by a harder material. The pin scars and the disc wear tracks for both pins were very similar (Figures 3 and 4, respectively). The  $\text{Al}_2\text{O}_3$  pin, with a much higher hardness (1100 HV), showed a slightly higher friction coefficient.

The disc wear coefficients (Table 1) corresponding to the three different pin materials were moderate/high ( $10^{-4} \text{ mm}^3/\text{N m}$ ), while the pins exhibited low wear ( $10^{-6} \text{ mm}^3/\text{N m}$ ). The X750 and 100Cr6 pins were protected by the lubrication provided by the coating whereas the  $\text{Al}_2\text{O}_3$  pin had low wear due to its high hardness, and therefore, as expected, showed better wear resistance.



Figure 1 Microstructure of HVOF TH103 coating as sprayed

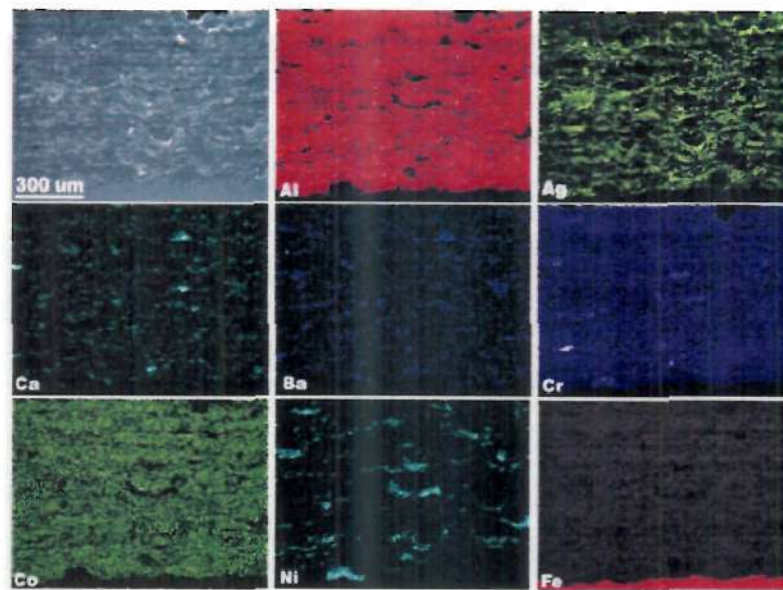


Figure 3 SEM-EDS mapping of the X750 pin scar (test carried out at 1 N normal applied load), showing transfer film with debris from the coating on the pin scar

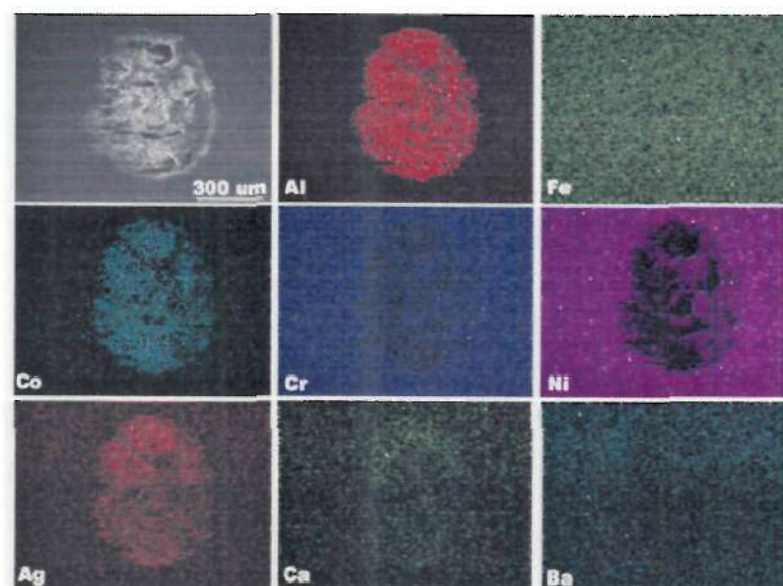


Figure 4 SEM-EDS mapping of the HVOF TH103 coating disc wear track after pin-on-disc tests in vacuum, showing no evidence of pin material on the disc

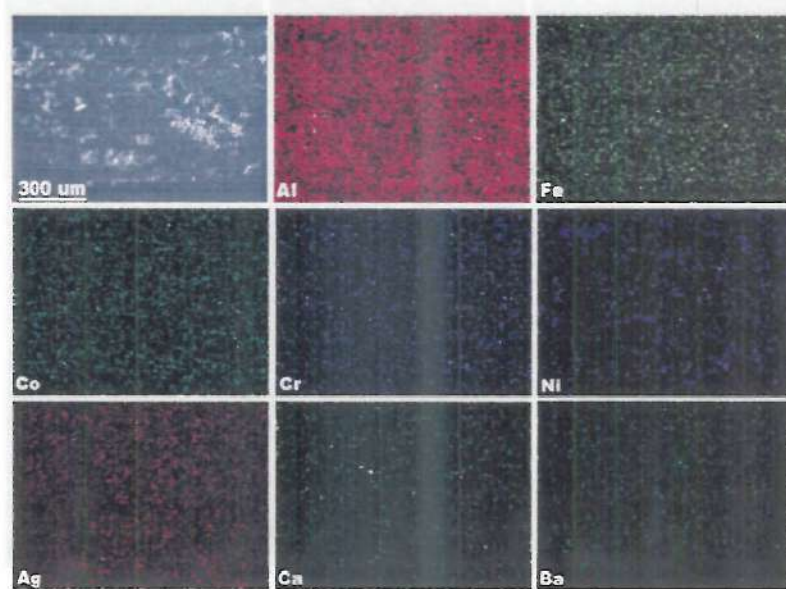
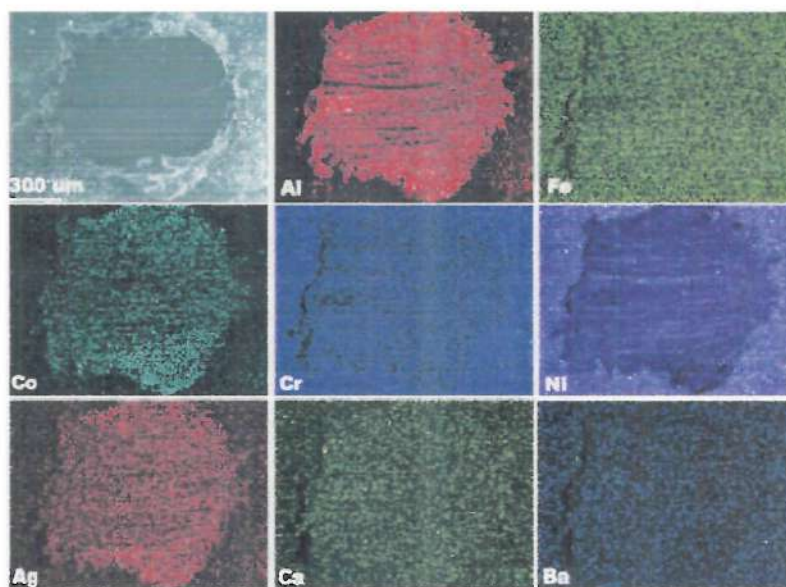
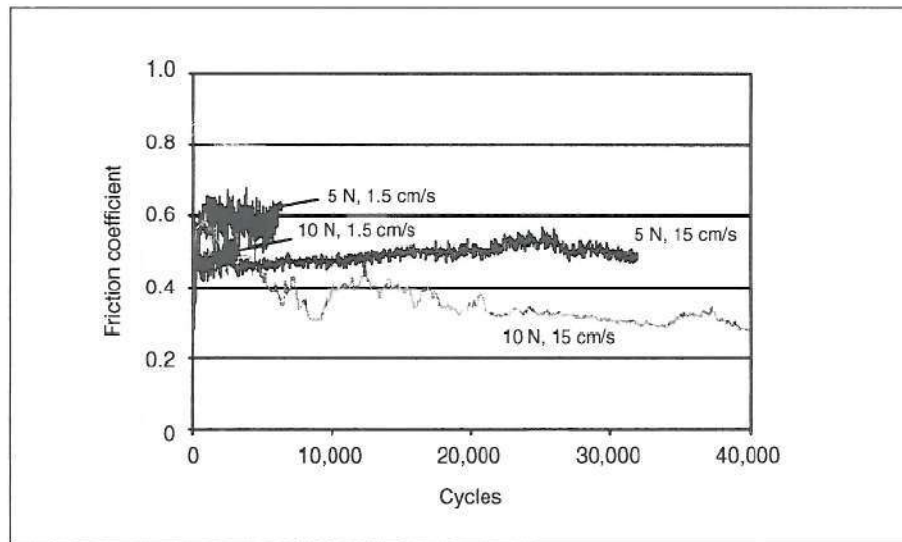


Figure 7 SEM-EDS mapping of the X750 pin scar from a test under 10 N load at 15 cm/s linear speed, showing complete transfer film without debris on the pin scar





**Figure 6 Influence of the linear speed on the friction coefficient for the HVOF TH103 coating and X750 pins at different loads under vacuum**



#### *Influence of linear speed*

The influence of the linear speed in tests using X750 pins at two different normal loads (5 and 10 N) is shown in **Figure 6**. Under a load of 5 N, increasing the linear speed resulted in a reduction of the friction coefficient, but the wear coefficients of both discs and pins remained very similar (moderate/high wear for the discs,  $10^{-4} \text{ mm}^3/\text{N m}$ , and moderate wear for the pins,  $10^{-5} \text{ mm}^3/\text{N m}$ ). Under a 10 N applied load, increasing the linear speed also caused a lower friction coefficient, which tended to decrease as a function of the number of cycles, reaching a value of 0.32 after 40,000 cycles. Moreover, the wear coefficients of both discs and pins were significantly reduced to moderate ( $10^{-5} \text{ mm}^3/\text{N m}$ ) and low ( $10^{-6} \text{ mm}^3/\text{N m}$ ), respectively.

A larger amount of lubricant material (see **Figure 7**, facing page, compared with **Figure 3**), transferred to the pin due to the higher pressure may account for the lower coefficients of friction and wear. Moreover, no pin material debris was found on the disc wear track. In addition, the higher speed will have been likely to cause a local increase in temperature, and previous results with this type of coating have shown a significant reduction in the friction coefficient at high temperatures.<sup>11</sup>

These results can be interpreted in terms of a mechanism implying an initial transfer of lubricant material from the coating to the pin until efficient

**Table 2** Disc wear track cross-sectional areas for the experiments carried out under 10 N load and at 15 cm/s speed as a function of the number of cycles

<i>Number of cycles</i>	<i>Disc wear track area (mm<sup>2</sup>)</i>
3,000	$1.2 \times 10^{-2}$
12,000	$3.7 \times 10^{-2}$
40,000	$3.0 \times 10^{-2}$

lubrication is obtained, explaining the reduction in the friction coefficient as a function of the number of cycles. Once the amount of transferred material is enough to cause good lubrication between the pin and the disc, the disc wear stops or becomes insignificant. Table 2 gives the disc wear track cross-sectional areas for the experiments carried out under a load of 10 N and at a speed of 15 cm/s as a function of the number of cycles. Initially, the wear track cross-section increases while coating material is being transferred from the disc to the pin. Then for 12,000 and 40,000 cycles there is no significant difference between the disc wear track cross-sectional area, indicating insignificant or undetectable wear of the disc.

## CONCLUSIONS

The results of pin-on-disc testing indicate that the HVOF TH103 self-lubricating QC composite coating improves the tribological behaviour of X750 and that it is a better self-lubricant in vacuum than under atmospheric pressure conditions. This is due to the generation of a transfer film over the pin scar under vacuum; at atmospheric pressure no transfer of material from the coating to the pin takes place and the coating behaves as a wear-resistant material rather than as a lubricant.

Increasing the normal applied load results in a reduction in the friction coefficient, probably due to the transfer of greater amounts of coating material from the disc to the pin or to a greater lubricated contact area.

Very hard pin materials such as  $\text{Al}_2\text{O}_3$ , with a hardness significantly higher than that of the coating, cause an increase in the friction coefficient of the TH103 coating.

A friction coefficient of 0.32 is attained under a 10 N applied normal load and at 15 cm/s linear speed after 40,000 cycles. The results are indicative of an initial coating transfer from the disc to the pin thereby coating the pin until very good lubrication is obtained. No significant disc wear takes place after the transfer of a critical amount of coating under these conditions.

In none of the tests carried out with the coated specimens did the wear scar reach the substrate material.

Future work will be focused on understanding the transfer mechanism in vacuum pin-on-disc tests and the possible influence of the oxygen content in the starting powders on the tribological properties of the coatings.

The best coatings obtained after terrestrial optimisation and qualification will eventually be tested in a tribometer (TriboLAB instrument) that will be integrated into the EuTEF on the International Space Station.

### Acknowledgements

---

The authors wish to acknowledge the valuable contribution from the personnel at the Metallic Materials Area of INTA. The vacuum pin-on-disc tests were carried out in the Aerospace and Space Materials Technology Test House - Austrian Research Centres (AMTT-ARC) in Seibersdorf, Austria, under MRI contract no. PRI-CT-1999-00024. This work was financed in part by the Spanish Ministry of Science and Technology of Spain under project PNE-008/2000-C-01.

### References

---

1. Roberts, F.W., Anderson, M.J., and Gould, S.G., *Protective Coatings and Thin Films*, Kluwer Academic, 1997, p. 135.
2. Oñate, J.I., Brizuela, M., García-Luis, A., Viviente, J.L., García de Blas, F.J., Agüero, A., Longo, F., and Román, A., 'Development and qualification of new solid lubricant coatings. A tribology experiment at the TriboLAB onto EuTEF', *Proc. 8th Int. Symp. on Materials in a Space Environment and 5th Int. Conf. on Protection of Materials and Structures from the LEO Space Environment*, Arcachon, France, 5-9 June 2000.
3. Anderson, M.J., and Roberts, F.W., 'An assessment of solid lubricant films for use in high temperature space applications', *ISA SP-334*, April 1993, pp. 379-84.
4. DellaCorte, C., 'The evaluation of a modified chrome oxide based high temperature solid lubricant coating for foil gas bearings', *Trib. Trans.*, **43**, 2 (2000) 257-62.
5. DellaCorte, C., and Fellenstein, J.A., 'Preliminary tuft testing of metallic bristles versus PS212, PS300 and HVOF300', *NASA TM-107522*, June 1998.
6. Stanford, M.K., and DellaCorte, C., 'Water atomization of barium fluoride-calcium fluoride for enhanced flow characteristics of PS304 feedstock powder blend', *NASA TM-2003-212125*, February 2003.
7. Kang, S.S., and Dubois, J.M., 'Compression testing of quasicrystalline materials', *Phil. Mag. B*, **66** (1992) 151.
8. Dubois, J.M., Kang, S.S., and Von Stebut, J., 'Quasicrystalline low-friction coatings', *J. Mater. Sci. Lett.*, **10** (1991) 537.
9. Lawn, B.R., and Howes, V.R., 'Elastic recovery at hardness indentations', *J. Mater. Sci.*, **16** (1981) 2745.
10. Sánchez, A., García de Blas, F.J., Algaba, J.M., Álvarez, J., Vallés, P., García-Poggio, M.C., and Agüero, A., 'Application of quasicrystalline materials as thermal barriers in aeronautics and future perspectives of use for these materials', *Mater. Res. Soc. Symp. Proc.*, **553** (1999) 447-58.
11. Román, A., Agüero, A., de Miguel, C., García de Blas, F.J., Longo, F., Muelas, R., and Sánchez, A., 'Characterisation of tribological quasicrystalline composite coatings', *Proc. Int. Thermal Spray Conf.*, Essen, Germany, 2002, pp. 419-23.
12. García de Blas, F.J., Agüero, A., Longo, F., Román, A., and Sánchez, A., 'High temperature self lubricant quasicrystalline composite coatings', poster presented at the *Int. Conf. on Metallurgical Coatings and Thin Films*, 30 April 2001.
13. Donnet, C., 'Advanced solid lubricant coatings for high vacuum environments', *Surf. Coat. Technol.*, **151-156** (1996) 80.
14. Fox, V.C., Renevier, J., Teer, D.G., Hampshire, J., and Rigato, V., 'The structure of tribologically improved MoS<sub>2</sub>-metal composite coatings and their industrial applications', *Surf. Coat. Technol.*, **116-119** (1999) 492-7.

This paper was first given at the 10th ESMATS Symposium, San Sebastian, Spain.